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ISRAEL INSTITUTE OF METALS

Non- Chromium Conversion Coatings on Aluminum

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Content	Page
1. Introduction	1
2. Background	1
3. Experimental	2
4. Results	4
4.1. Deposition from zirconate solutions	4
4.2 Deposition from molybdate solutions	7
4.3. Deposition from zinc phosphate solution under external polarization	8
5. Summary	11
6. References	12
7. Illustrations	13

1. Introduction

This investigation is the 3-d Phase of the work devoted to the development of alternatives for chromium passivation of Al alloys.

In Phases 1 and 2 of the work our efforts were concentrated on non-chromate passivation of Al 2024-T3. Our results showed that it was impossible to produce effective protective coating on Al 2024 by means of conversion process, mainly, because of non-homogeneous structure of the material. Along with this the deposition from a zinc/phosphate solution under an external cathodic polarization was proposed as a replacement of chromate passivation of Al 2024 T3. The work conducted in Phases 1 and 2 of the investigation allowed to develop a laboratory process providing passivation of Al 2024 T3. Protective coatings produced according to the developed process exhibited good corrosion resistance (more than 300 hour salt spray test) and paintability and could be considered as alternative to chromium conversion coatings [1].

This stage of the work was devoted to passivation of Al 7075. This material contains in average 1.6 % Cu, 2.5 % Mg and 5,6 % Zn. Intermetallics which can be formed by these elements are as follows: $MgZn_2$, $CuAl_2$, Mg_2Al_3 or Mg_5Al_8 , $CuMgAl_2$ or $Cu_2Mg_2Al_5$ and $Cu MgAl$. $MgZn_2$ is the principal soluble phase precipitated in Al 7075 as a result of tempering, but others may also be present [2]. Al 7075 is susceptible to general and localized (pitting and intergranular) corrosion. $MgZn_2$ is anodic to the matrix [3]. Its precipitation in the grain boundaries contributes to the formation of anodic path in the vicinity of grain boundaries [4]. In addition, another location of the anodic path appears to be the copper-depleted bands along the grain boundaries [5].

2. Background.

Permanganate Passivation [1], modified Ce-permanganate process [2], passivation comprising a treatment in trivalent chromium solution [3], modified cerium-molybdate process [4] were applied for treatment of Al 7075. These processes provided the results comparable in corrosion resistance with those of chromate passivation. However, they suffer from some disadvantages. All of them are multistage processes and are characterized by long duration and usage of high temperatures. These conditions are impractical for industrial use especially for treating of assembled aircraft.

It should be noted that none of the processes which provided acceptable results was a simple conversion process. Combination of different treatments allowed to achieve considerable enhancement of corrosion resistance probably due to synergistic effect of different factors.

During recent years an extensive investigation was done in order to develop alternative processes for chromium passivation. Good results were obtained using mixtures of fluoroacids with polymeric compounds. It was shown that the choice of fluoacid and polymer in the treatment had strong impact on coating performance [10].

Mo- containing coating was deposited on aluminum without the use of external polarization, but using a buffer and a complexant. Optimal coating was produced having a pitting resistance comparable to that of chromate conversion coatings [11].

During the past few years there has been a strong interest in developing conductive polymers as an alternative to the traditional anticorrosion coatings. A double strand polyaniline molecular complex was used as a coating material on Al 7075 - T6. Potentiodynamic tests indicated effectiveness of the coatings for protection against corrosion [12].

The literature data showed that the coatings comprising polymeric species were promising for passivation of aluminum.

We studied feasibility of application of molybdate /phosphate and zirconate conversion coatings deposited in the presence of N-containing organic additives and of zinc/phosphate coatings deposited under external polarization.

3. Experimental

Al 7075 specimens of dimensions 2x5 cm were degreased chemically and rinsed with de-ionized water. The composition of the degreasing solution is shown in Table 1. Temperature and time were 50°C and 10 min, respectively. After rinsing, the samples were immediately immersed in zirconate or molybdate passivation solutions.

Compositions of the passivation solutions are shown in Table 2.

Table 1. Solution for degreasing.

Component	Content, %
Sodium metasilicate	3
NaH_2PO_4	1.2
Na_3PO_4	2.5.
Soap	2

Table 2. Compositions of passivation solutions.

	Component	Concentration, g/l		
		Solution 1	Solution 2	Solution 3
Zirconate solutions	$\text{Zr}(\text{OH})_2(\text{NO}_3)_2$	2	0.2	0.2
	NaNO_3	20	20	2.0
	H_3BO_3	5	5	0,5
	KHF_2	1	1	1
Molybdate solution	$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	6		
	$\text{Na}_2 \text{ Si O}_3 \cdot 5\text{H}_2\text{O}$	6		
	$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$	6		

N-containing polymers which were used as additives in these solutions were as follows:

- * polyaniline in the form of water suspension stabilized by sodium lauryl sulphate (SLS) . Content of polyaniline in suspension was 1.6 % and molar ratio polyaniline : SLS was 1:1 ;
- * polyethyleneimine with molecular weight 2000;
- *Merquant 100 (polydiallyldimethyl ammonium chloride).

Deposition of phosphate coating under external polarization was carried out using solution and conditions listed in Table 3.

The effectiveness of the passivation procedures was estimated by salt spray test according ASTM B 117 in a salt spray cabinet NOA, ISO 002. The samples were

checked every 24 h and test continued till appearance of a few small corrosion spots on the surface of the sample. Microstructure of the deposited layers was examined using Scanning Electron Microscopy. Composition of coatings was determined by Energy Dispersive Analysis System (EDS).

Table 3. Solution and deposition conditions for production of phosphate coating.

Solution composition	Deposition conditions
H ₃ PO ₄ - 8 ml/L	60°C
HNO ₃ - 3- 4 ml/L	0.75-1.0 A/dm ²
ZnCO ₃ - 6 g/L	13 min.
	Zinc anode

4. Results.

4.1. Deposition from zirconate solutions.

Table 4 illustrates the effect of composition of zirconate solution and deposition conditions on visual view and corrosion resistance of conversion coatings on Al 7075.

The increase of Zr(OH)₂(NO₃)₂ concentration in the solution, immersion temperature and pH contributed to the increase of corrosion resistance of the films. However, pits and stains of white corrosion could be seen even on the surface of the best films (produced from the solution with 2 g/l Zr(OH)₂(NO₃)₂ at 50°C for 1-5 min). On the other hand the treatment in zirconate solution provided noticeable improvement of corrosion resistance. The surface of untreated samples was covered with corrosion stains already after 2-3 h salt spray test. On the surface of the samples treated in zirconate solution N 1 localized corrosion appeared after 24 h salt spray test.

Effect of N-containing organic additives in concentrated (2 g/l Zr(OH)₂(NO₃)₂, N 1) and diluted (0.2 g/l Zr(OH)₂(NO₃)₂, N 2 and 3) zirconate solutions is shown in Tables 5 and 6, respectively.

Table 4. Effect of composition of zirconate solution and deposition conditions on general view and corrosion resistance of conversion coatings.

No	Deposition conditions			General view of film	Results of 24 h corrosion test
	pH	T°,C	Duration, min		
1	2.4	25	1	Yellow film	Very hard black corrosion on the entire surface of the sample
		50	1	Yellow-violet film	Pits and stains of white corrosion
		50	5	Yellow-violet film	Pits and stains of white corrosion
	1.4	50	5	No visible film	Intensive black corrosion on the entire surface of the sample
2	3.9	50	1	Yellow film	Intensive black-brown corrosion on the entire surface of the sample
3	3.5	50	1	Yellow film	Deep pits and a lot of large stains of black-brown corrosion
	2.4	50	1	No visible film	A lot of large stains of black-brown corrosion

Table 5. Effect of N-containing organic additives on view and corrosion resistance of conversion films deposited from concentrated zirconate solution.

Additive	Concentration, g/l	View of film	Results of 24 h corrosion test
Polyaniline suspension	1.5	Violet film	Pitting corrosion
	3.0	Yellow-violet film	Few pits near edges
	5.0	No visible film	Slight pitting corrosion
Merquat 100	5	Light-yellow film	Stains of corrosion
	15		

Note: Deposition at pH 2.4, 50°C, 5 min.

The data in Table 4,5 show that the presence of polyaniline suspension in amount of 3.0 g/l in the zirconate solution slightly increased the protective properties of zirconate films. However corrosion resistance of deposited films was insufficient and decreased when concentration of polyaniline suspension increased up to 5.0 g/l.

Polyaniline suspension contained stabilizing surfactant (SLS) along with polyaniline. The increase of SLS concentration might be the reason of the decrease of protective properties of the films. Presumably, passivation effect of polyaniline additive could be better if it was in a soluble form but not in the form of suspension.

The increase of the duration of salt spray test to 48 h resulted in considerable pitting corrosion even of the best samples prepared using additives of polyaniline suspension.

Table 6. Effect of polyimine additives on view and corrosion resistance of conversion films deposited from diluted zirconate solution.

Polyethylenimine concentration, g/l	View of film	Results of 24 h corrosion test
0.5	Light-yellow film	Many stains of corrosion
1.0	No visible film	
2.5	No visible film	Few black corr. stains

Note: Deposition at pH 3.9, 50°C, 1 min.

Additives of Merquat 100 did not exhibit any positive effect on corrosion resistance of zirconate conversion films.

Polyethylenimine even with low molecular weight 2000 was insoluble in concentrated zirconate solution, but it was dissolved in diluted zirconate solution up to concentration of 2.5 g/l. So additives of polyethylenimine (molecular weight 2000) were introduced only in diluted solution (See Table 6). Noticeable improvement of corrosion protection in 24 h salt spray test was achieved using polyethylenimine additive in the concentration of 2.5 g/l. The increase of test duration to 48 h showed intensive attack of general corrosion on the surface of the samples passivated with polyethylenimine additives.

The results showed that some N-containing polymeric additives in zirconate solution could be effective for improvement of corrosion resistance of zirconate conversion films, however, in order to achieve satisfactory results, the optimization of zirconate solution composition and N-containing polymer structure is necessary.

Morphology and composition of the unpassivated sample and samples passivated in solutions N1 and 2 after corrosion test are shown in Figs. 1-3. Uncoated surface (Fig.1) was attacked strongly after 2.5 h as compared to coated samples after 48 h

corrosion test (Figs. 2 and 3). On the surface of the sample passivated in zirconate solution N 1 the local corrosion was developed (Fig. 3, p. 8, 9, 10). EDS analysis of protected and unprotected surfaces revealed that the main elements were O, Al, Mg, Zn and Cu. In all cases could be seen non uniform distribution of elements, particularly of O over the surface, that indicated non uniform development of corrosion process. Zr and F were revealed in concentrations lower than 1 % on passivated surfaces; the concentrations of these elements were lower than the level of detection in a number of points (Tables in Figs. 2 and 3). The results showed that treatment in zirconate solutions led to the formation of thin films. Protective ability of these films was insufficient, presumably, because of their non uniformity in thickness and composition.

Average contents of Cu and Zn on passivated and unprotected surfaces were different. Cu content decreased from 1.95 –3.41 % to 0.64-3.47 % and 0.41-1.88 % in the sequence of the surfaces unpassivated, passivated in diluted solution N2 and passivated in concentrated solution N1. In opposite, Zn content varied in the ranges of 0.52-1.88 % and 1.71-2.53 % for unpassivated and passivated surfaces, respectively. At this stage of the work it is impossible to reveal the reason for the changes in composition. They could be associated either with passivation or as a result of the corrosion during salt spray test. To investigate these processes, more work should be done, particularly the structure and composition of as deposited passive films should be studied.

4.2. Deposition from molybdate solution.

General view of molybdate films on Al 7075 and their corrosion resistance in dependence on deposition conditions are shown in Table 7.

As could be seen, the treatment in molybdate solution at conditions which are shown in Table 7 did not provide corrosion protection for Al 7075. Experiments to introduce N-containing polymeric additives in the molybdate solution were unsuccessful, because of their insolubility. Besides, they caused the decomposition of the solution.

Deposition in the presence of N-containing low molecular additive benzotriazol did not lead to improvement of corrosion resistance of the molybdate film.

Table 7. Effect of deposition conditions and additives in molybdate solution on general view and corrosion resistance of conversion coatings.

Deposition conditions				View of film	Results of 24 h corrosion test
pH	Dur, min	Additive	Conc., g/l		
11	5	-	-	No visible film	Large brown corrosion stains on the entire surface of the samples
		KHF ₂	1,0		
6		KHF ₂	2	Light yellow film	
		KHF ₂	3.5	Golden yellow film	
	10			Red violet film	
	5	KHF ₂	3.5	Light yellow film	
	10	Benzotriazol	1.5	Violet film	

Note: Deposition at 25°C.

Morphology and composition of the surface passivated in the molybdate solution are shown in Fig. 4. Morphology of the passivated in the molybdate solution surface was very similar to that of unpassivated surface and surfaces passivated in zirconate solutions. Cu and Zn concentrations were lower and higher, respectively than those on an unpassivated surface. Points 1 and 2 were located in the area without hard corrosion damage, while points 3 and 4 in the area of large brown corrosion stains. In points 1 and 2 the low concentrations of Mo and F (lower than 1 %) were revealed. In the area of corrosion (points 3 and 4) concentration of these elements was lower than the detection level . Along with this some increase of Al content was observed. The results showed that treatment of Al 7075 in molybdate solution resulted in the formation of Mo- and F- containing film; this film was destroyed in corrosion test.

4.3. Deposition from zinc/phosphate solution under external polarization.

Table 8 illustrates the effect of additives in zinc/ phosphate solution and current density on view and corrosion resistance of zinc/phosphate coatings. Coatings deposited at all investigated conditions exhibited relatively high corrosion resistance. Samples 49, 50, 51 withstood 168 h corrosion salt spray test. It should be emphasized that the coatings had non uniformity in thickness. The rate of coatings growth was considerably higher at the edges of the samples than in the center and increased with

considerably higher at the edges of the samples than in the center and increased with the distance from the electrolyte upper level, which played the role of a screen for current flow. Non uniformity in thickness of the coatings which were deposited on Al 7075 was considerably higher than that found in previous work on Al 2024.

As the rate of phosphate coating deposition is expected to increase with the increase in intensity of hydrogen evolution, it could be supposed that the difference in the degree of coating uniformity on Al 2024 and Al7075 was associated with the influence of the substrate on hydrogen evolution process. Effect of potential on the rate of hydrogen evolution was presumably stronger for Al 7075 substrate than for Al 2024 one. High non uniformity of coating thickness did not allow to produce coatings of desirable thickness on the entire surface of the sample. The data shown in Table 8 are related to the central area of the samples. The changes in the solution composition and deposition conditions did not improve coating uniformity.

The morphology of zinc phosphate coatings after 168 h corrosion test in the areas without and with corrosion damage is shown in Figs. 5-7 and 8, 9, respectively. The composition of the areas which were not damaged by corrosion are shown in Table 9.

Table 8. Effect of additives in zinc/ phosphate solution and current density on view and corrosion resistance of zinc/phosphate coatings. Deposition time was 13 min.

No	Pretreatment	Additive	Conc., g/l	Dc, A/dm ²	View	Results of 168 h salt spray
42	30 % H ₃ PO ₄ , 25°C, 3 min	No additives	-	0.75	Light gray coating	A few spots after 24 h test; no additional spots after 168 h test
47		H ₃ BO ₃	30			Corrosion area after 24 h test; no additional spots after 168 h test
49		MgSO ₄	25		Dark gray coating	One spot after 48 h and 3 spots after 96 h; no additional spots after 168 h test
50	Without special pretreatment	H ₃ BO ₃	30	1.00	Light gray	2 corrosion spots
51					coating	No corrosion

Table 9. Composition of zinc/ phosphate coatings in the areas which were not damaged by corrosion.

Element	Content, % (a.c.)			
	Sample 42	Sample 47	Sample 49	Sample 50
O	64.27	66.57	69.57	66.44
Mg	-	-	4.03	-
Al	4.52	9.00	0.58	0.68
P	12.30	9.42	12.00	12.38
Zn	18.91	15.01	13.83	20.49

Note: Samples after 168 h corrosion salt spray test.

Figs.5 and 7 showed that zinc phosphate coating consisted of the large needle like crystals (dendrites) and crystals of irregular form (sished 1 and 2).

The introduction of H_3BO_4 in zinc phosphate electrolyte did not led to principal change of the morphology of coatings (Figs 5 a and b), however size and amounts of two types of crystals were different. The crystals of non regular form in the coating deposited with H_3BO_4 (Sample 47) were finer than in the coating deposited without H_3BO_4 (Sample 42). In the later coating a less amount of dendrites was observed. Elimination of the sample pretreatment in H_3PO_4 (Sample 50) also did not change type of the coating morphology, however the size and relative amount of the crystals of irregular form increased (Fig.7). As could be seen from the data in Fig. deposition of the coating in the presence of $MgSO_4$ (Sample 49) resulted in a considerable change in surface morphology. This coating consisted of relatively small (about 5-10 μm) cubic crystals regularly arranged in flower like coalescences, while dendrites were disappeared.

Data in Table 9 showed that all investigated phosphate coatings contained Al along with Zn, O, P. Introduction of $MgSO_4$ in the electrolyte resulted in the incorporation of Mg in the coating composition.

The content of Al was lower than 1 % in coatings that exhibited high protective properties, while it reached 5-9 % in the coatings exhibited insufficient protective ability. The increase in Al content could be a sign of the beginning of the corrosion

process. The Al content on the surface of Samples 42 and 47 in the areas with corrosion damage was even considerably higher (up to 30 %, see Figs. 8 and 9). As it was shown in our previous report [14], high concentration of Al in phosphate coating was associated with inadequate pretreatment of the substrate and being reduced with the increase of coating thickness. Therefore high content of Al in the coatings on Samples 42 and 47 might be due to their thickness insufficient for effective corrosion protection. Pretreatment in H_3PO_4 also might contribute to the increased Al content.

The obtained results showed that zinc phosphate coatings deposited under external polarization was the best passivation process for corrosion protection of Al 7075. However, localized corrosion was observed in some areas of the samples likely because of non uniformity and defects in the coatings.

In order to reveal the technological parameters influencing the coating composition, structure, integrity and protection ability it is necessary to investigate in details the deposition of phosphate coating on Al 7075 and analyze the characteristics as deposited and subjected to the corrosion test coatings.

5. Summary

* Al 7075 was treated in zirconate and molybdate phosphate solutions with and without N-containing organic additives. On the surface of the samples treated in zirconate and molybdate solutions Zr, F and Mo, F, respectively, were revealed in low concentrations (lower than 1 %). Treatment in molybdate solution did not improve corrosion resistance of the samples. Treatment in zirconate solutions provided some passivation of the aluminum surface (localized corrosion appeared after 24 h salt spray test, while the surface of untreated samples was highly corroded after 2-3 hrs test). Introducing of N-containing polymeric additives in the solution composition contributed to the improvement of protective ability of the formed conversion films. Treatment in zirconate solutions with N-containing organic compounds, presumably, is one of the promising directions of passivation of Al 7075.

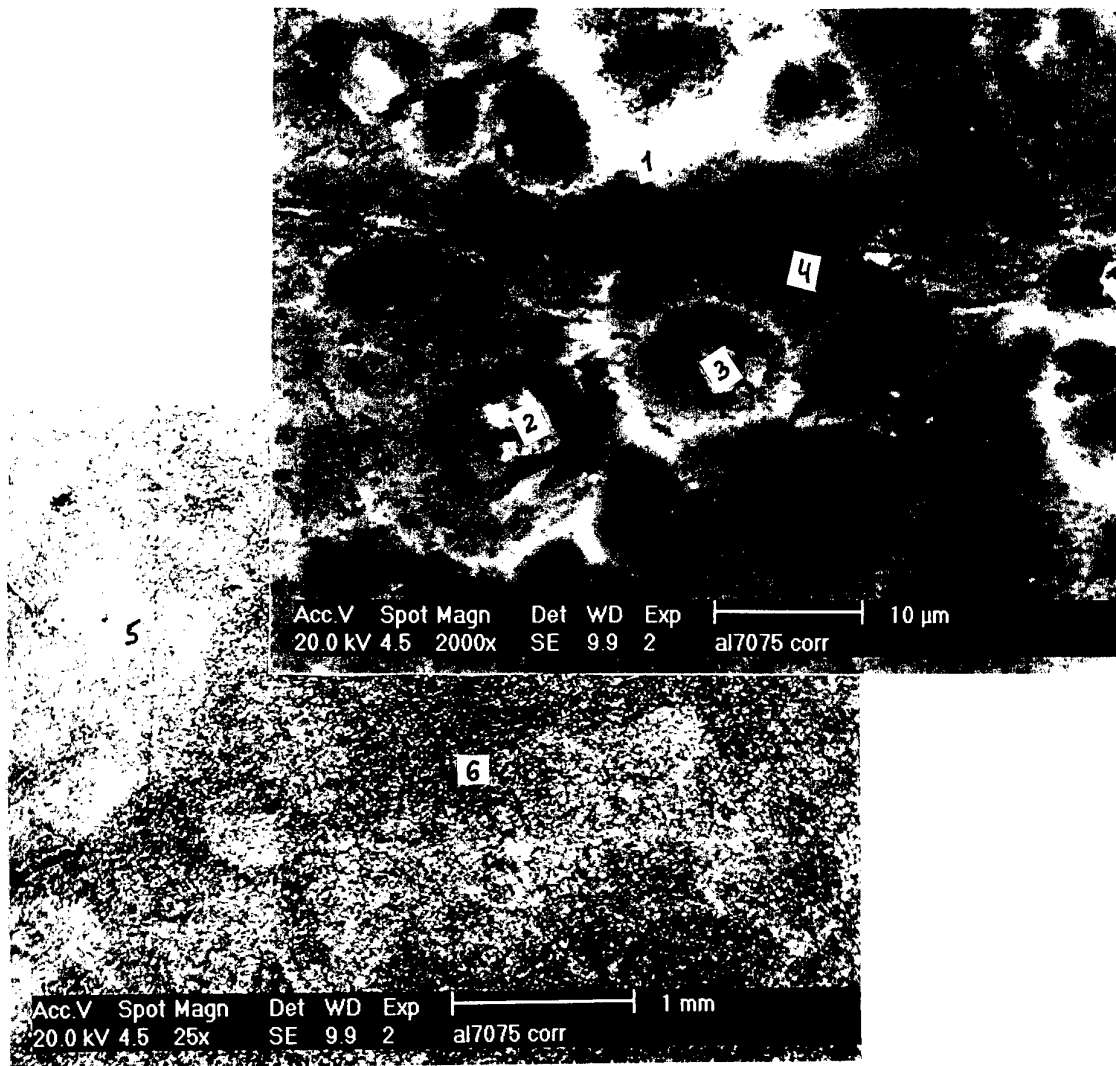
* Zinc phosphate coatings were deposited on Al 7075 under external polarization. Coatings consisted of the crystals of irregular form and dendrites with composition 13-20 % Zn, 9-12 % P, 64-69 % O and up to 9 % Al. A few samples with these

coatings withstood 168 h corrosion salt spray test according to ASTM B 117, while on others localized corrosion was revealed. In order to obtain reproducible and reliable results, the relationship between deposition conditions, composition, structure and protective ability of phosphate coatings on Al 7075 should be investigated.

6. References

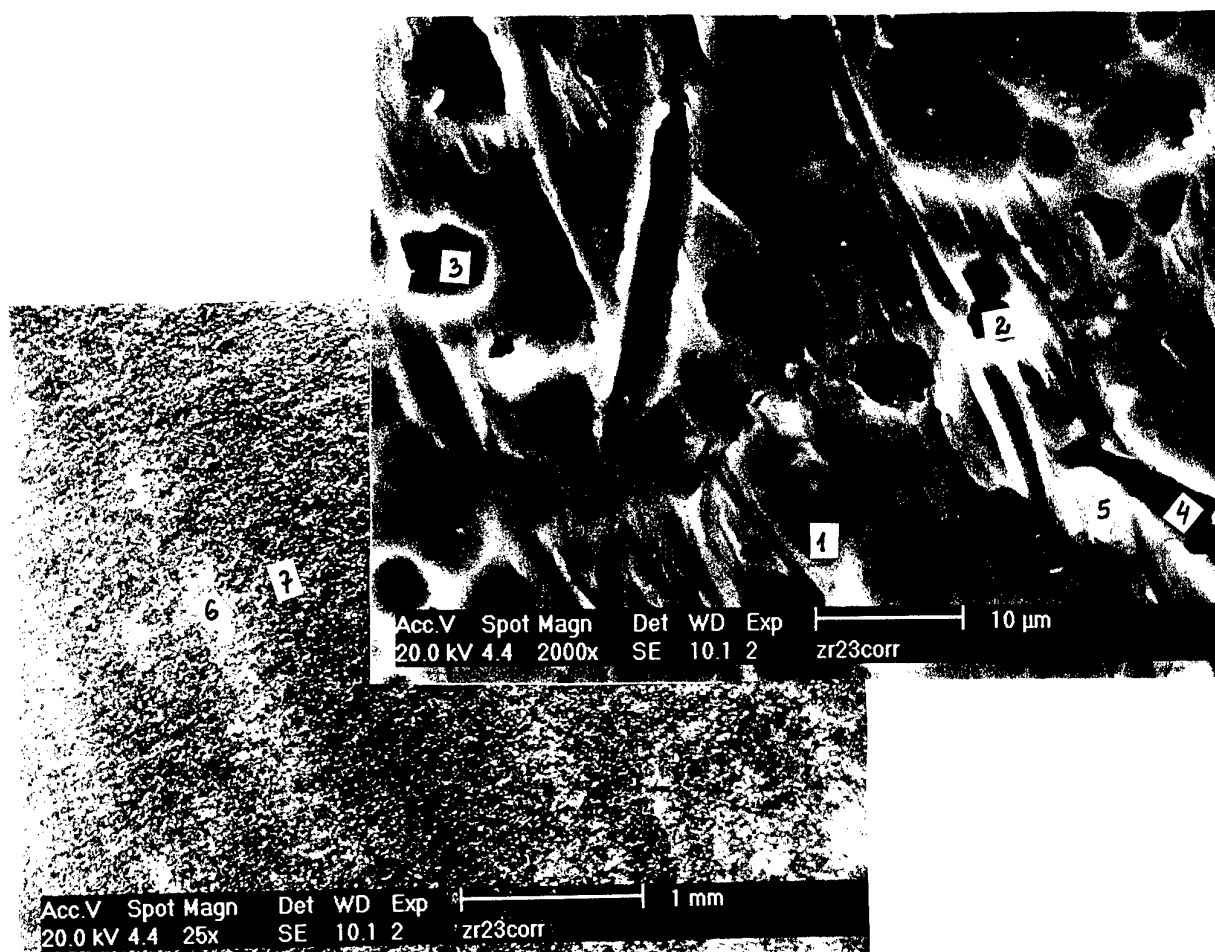
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7. Illustrations.



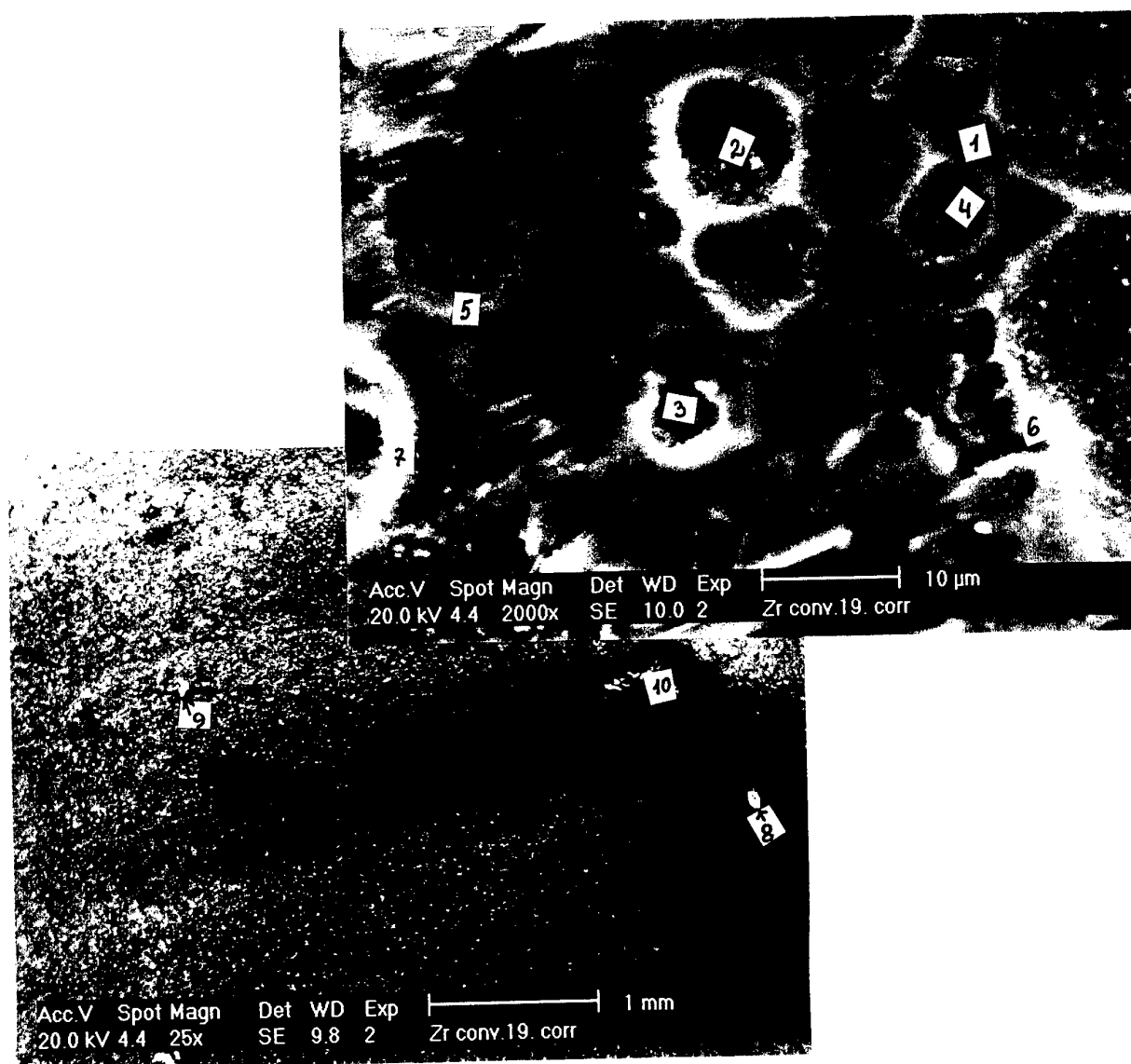
Element	Content, % (a.c.)					
	1	2	3	4	5	6
O	15.33	3.42	1.37	7.91	24.46	8.25
Mg	2.31	1.82	1.53	2.34	1.46	2.26
Al	79.89	89.69	92.20	86.26	70.07	86.12
Zn	0.52	1.67	1.88	0.80	0.84	0.63
Cu	1.95	3.41	3.02	2.70	3.20	2.73

Fig. 1. Morphology of base surface Al 7075 without passivation after 2.5 h corrosion test and composition of the surface in different points.



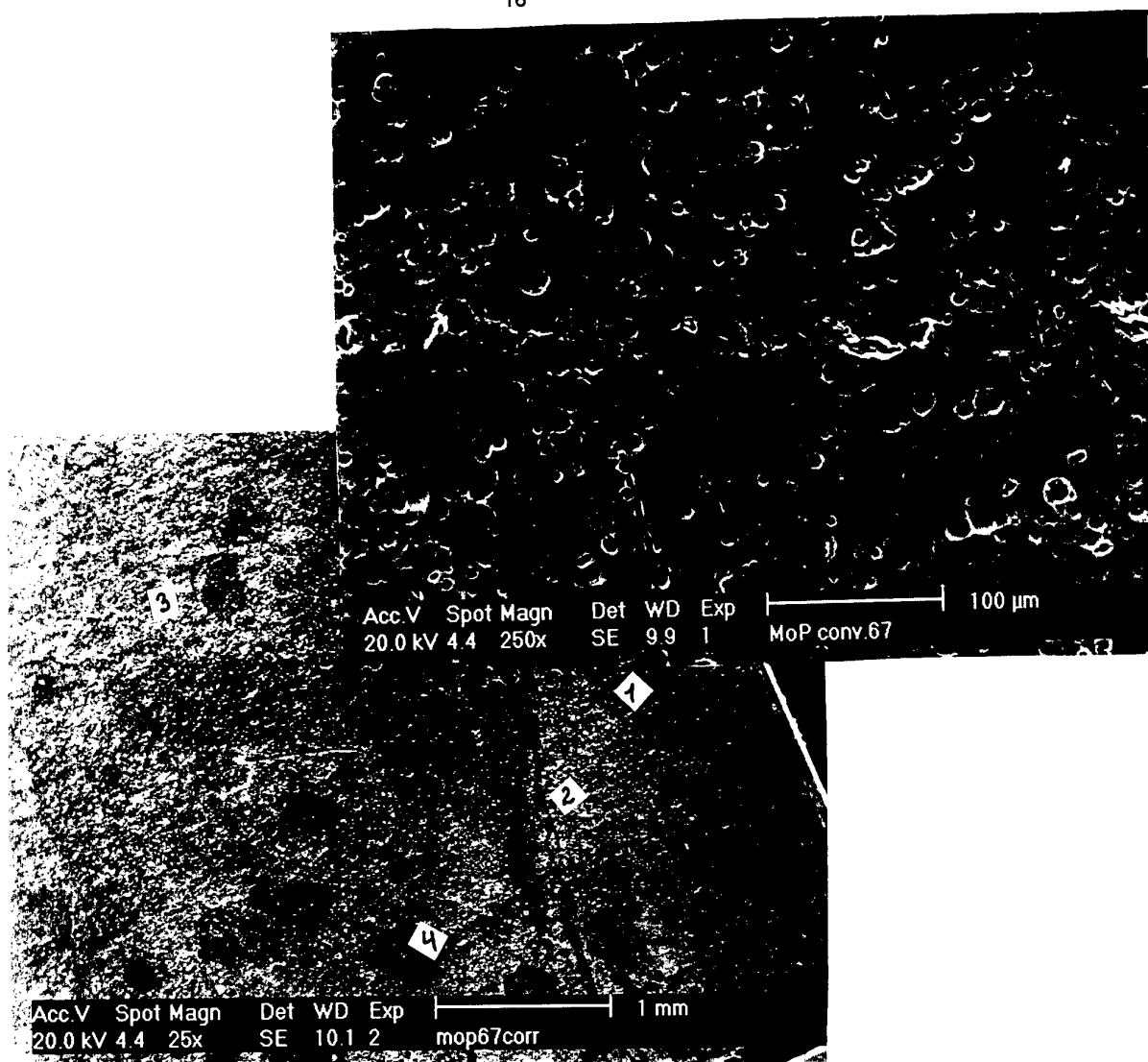
Element	Content, % (a.c.)						
	1	2	3	4	5	6	7
O	5.38	2.47	5.00	22.65	12.30	5.75	6.62
F	0.22*	0.01	0.41*	0.21*	0.42*	0.14*	0.86
Mg	2.19	2.09	2.32	1.80	2.26	2.41	2.53
Al	89.11	87.54	88.24	70.54	82.07	87.98	86.68
Si	0.13*	0.54	0.17*	0.82	0.37	0.24	0.26
Cu	0.64	3.47	0.87	0.99	0.60	0.76	0.70
Zn	2.33	3.94	2.99	2.99	1.97	2.66	2.33
Zr	0.00*	-0.05*	0.00*	-0.01*	0.01*	0.07*	0.02*

Fig. 2. Surface morphology of Al 7075 after 48 h corrosion test and composition of the surface in different points. Passivation was done in zirconate solution N 2 with 2.5 g/l polyethylenimine at pH 3.9, 50 °C, 1 min.



Element	Content, % (a.c.)									
	1	2	3	4	5	6	7	8	9	10
O	15.66	19.41	12.13	21.11	15.37	22.42	43.86	20.72	20.58	32.24
F	0.35*	0.83	0.02*	0.34*	0.48*	1.03	0.61*	0.44*	0.35*	0.53*
Mg	1.98	1.85	1.71	1.75	2.05	1.88	1.09	1.91	1.80	1.84
Al	78.50	73.72	80.26	72.66	78.47	71.66	50.91	73.46	73.88	62.23
Si	0.60	0.67	0.56	0.60	0.56	0.63	0.96	0.66	0.56	0.99
Cu	0.67	0.57	1.08	0.75	0.69	0.41	0.51	0.64	0.62	0.47
Zn	2.05	2.53	3.92	2.35	2.19	1.70	1.79	1.86	1.96	1.57
Zr	0.19	0.43	0.31	0.46	0.20	0.27	0.28	0.29	0.24	0.12

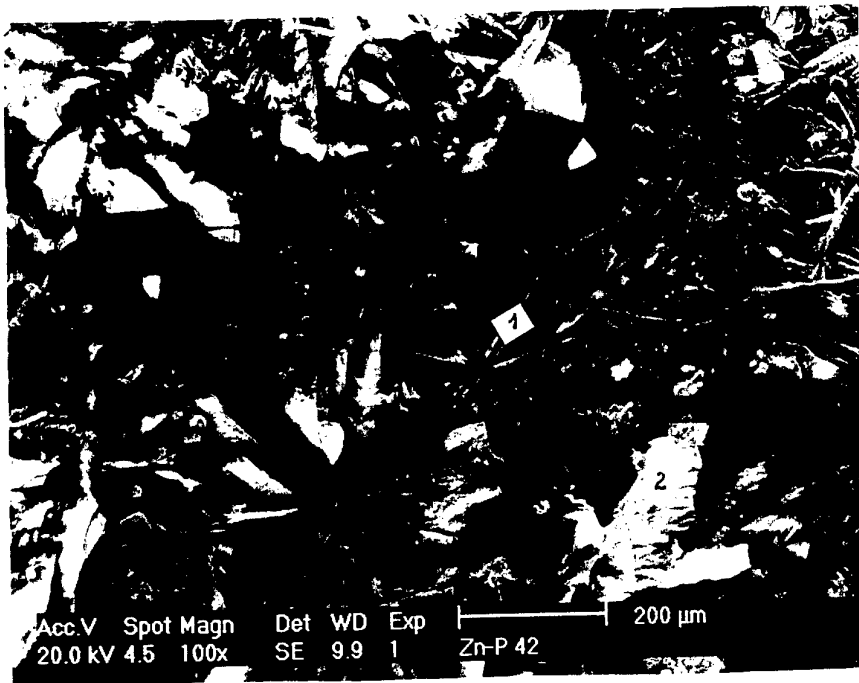
Fig. 3. Surface morphology of Al 7075 after 48 h corrosion test and composition of the surface in different points. Passivation was done in zirconate solution N 1 with 3.0 g/l polyaniline suspension at pH 2.4, 50°C, 5 min.



Element	Content, % (a.c.)			
	1	2	3	4
O	16.62	25.53	10.50	17.62
F	1.47	0.84	0.42*	0.23*
Mg	2.09	1.63	2.23	2.19
Al	75.99	68.41	83.12	77.31
Si	0.22	0.44	0.22*	0.13*
P	0.02	0.28	0.04*	0.08*
Cu	1.07	0.51	0.65	0.50
Zn	2.27	2.06	2.76	1.98
Mo	0.24	0.31	0.07	-0.03*

Fig. 4. Surface morphology of Al 7075 after 48 h corrosion test and composition of the surface in different points. Passivation was done in molybdate solution at pH 6.0, 25 °C, 5 min.

a



b

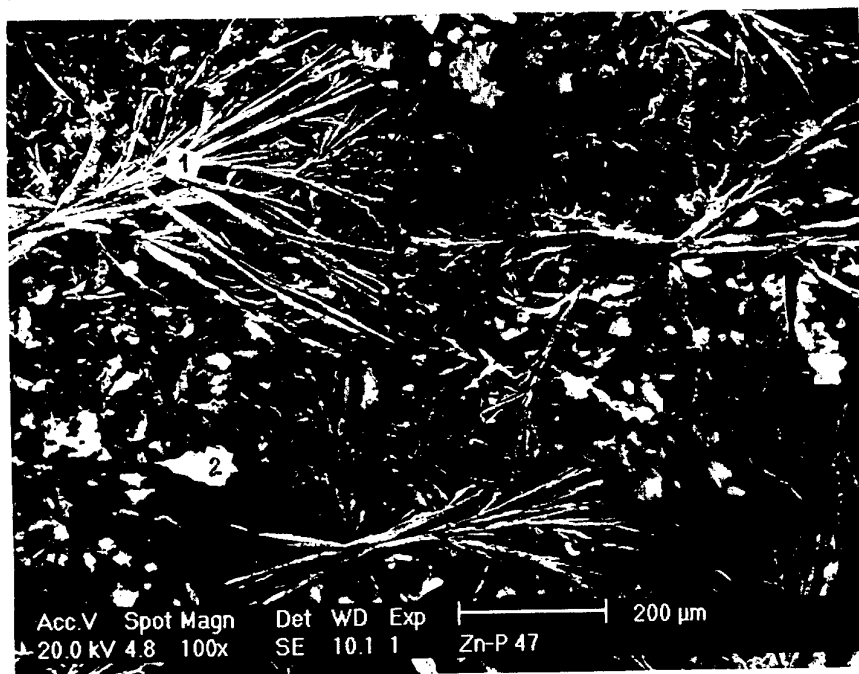


Fig. 5. Surface morphology (as observed by SEM) of zinc phosphate coatings after 168 h corrosion test in the area without corrosion damage. a- Sample 42, b- Sample 47.

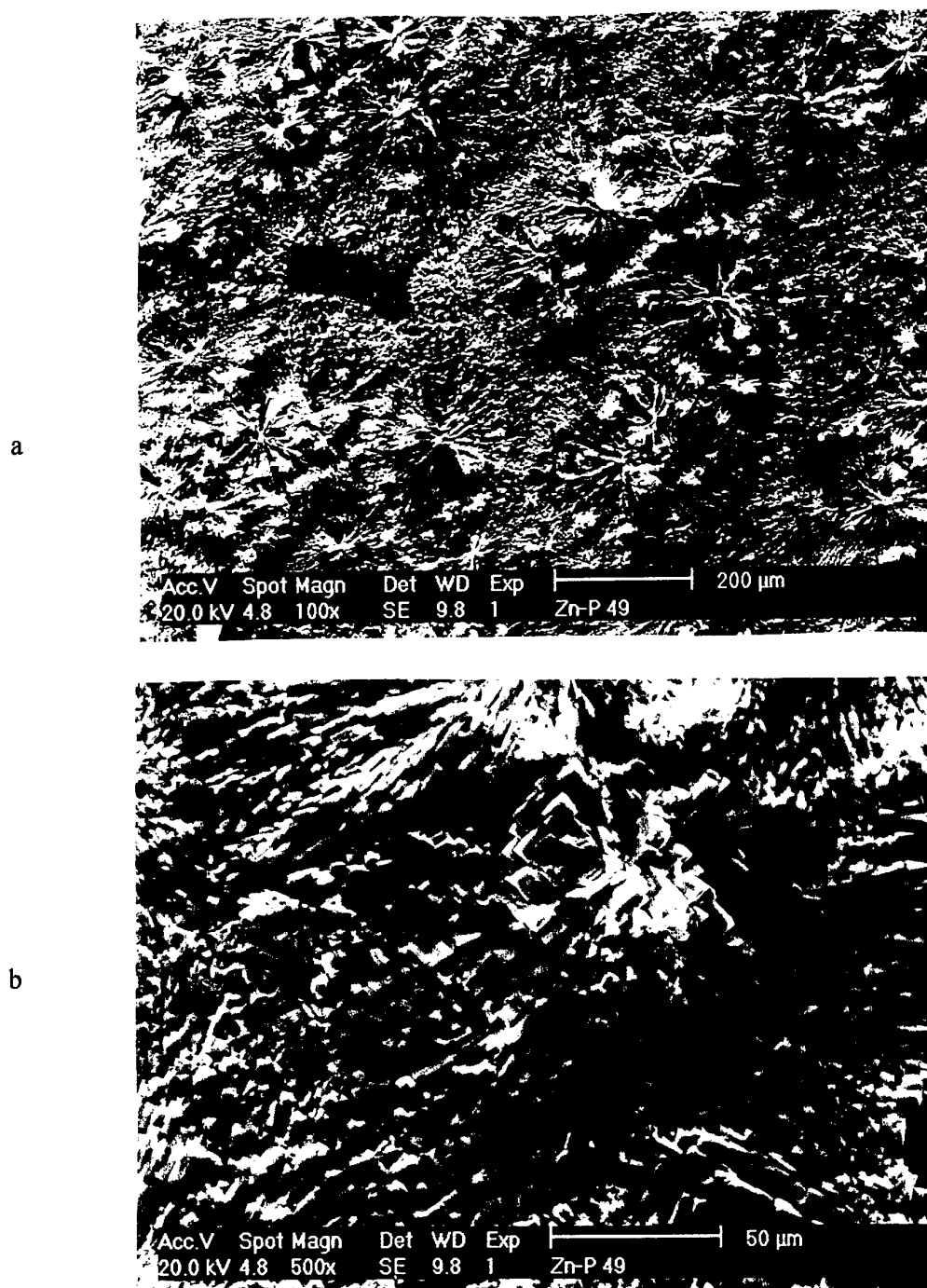


Fig. 6. Surface morphology of zinc phosphate coatings after 168 h corrosion test in the area without corrosion damage. Sample 49. a- magnification 100; b- magnification 500.

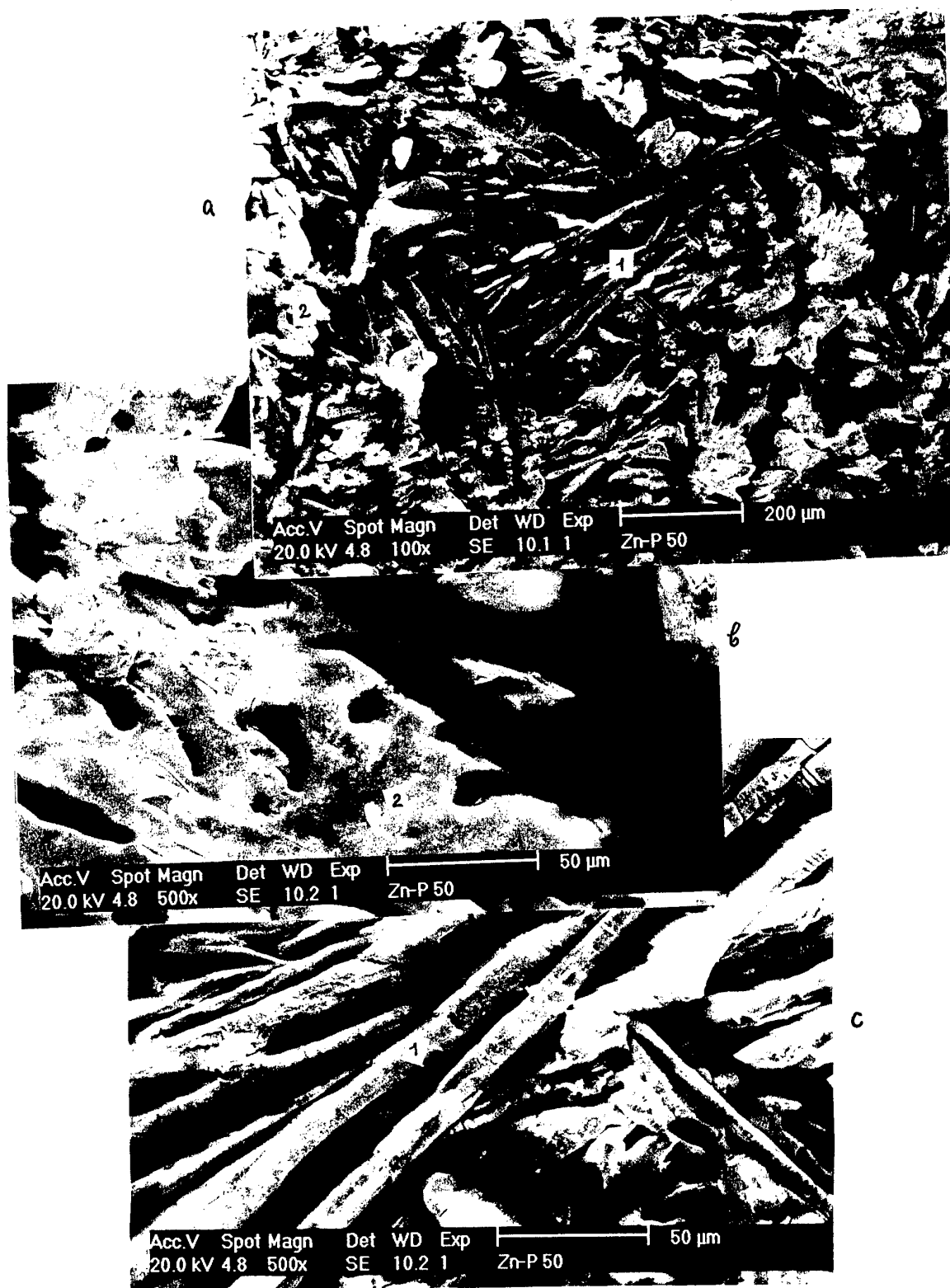
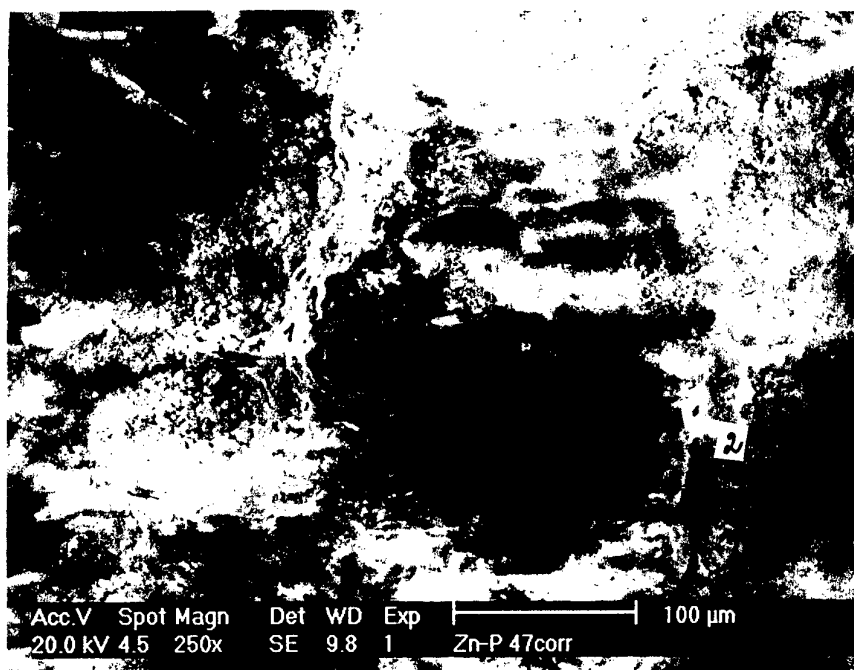


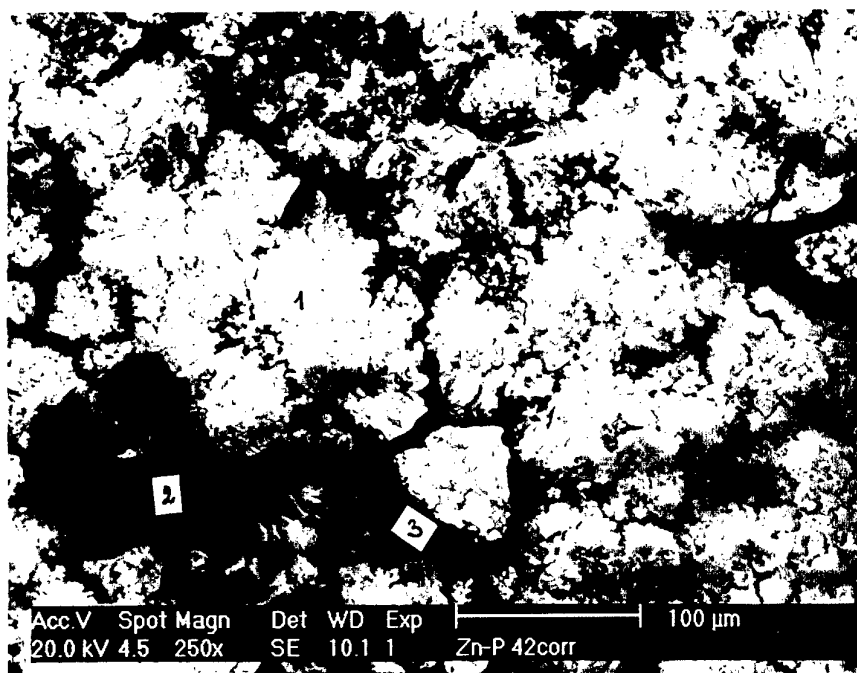
Fig. 7. Surface morphology of zinc phosphate coatings after 168 h corrosion test in the area without corrosion damage. Sample 50. a-magnification 100; b and c – magnification 500; b- crystals of irregular form. c- dendrites.



Composition of the surface in different points:

Element	Content, % (a.c.)		
	1	2	3
O	68.33	58.36	44.12
Al	24.09	23.04	12.70
P	3.62	7.94	2.05
Zn	3.97	10.65	41.12

Fig. 8. Surface morphology of the area with corrosion damage . Sample 42.



Composition of the surface in different points:

Element	Content, % (a.c.)	
	1	2
O	68.57	66.22
Al	29.10	31.18
P	0.64	0.87
Zn	1.69	1.73

Fig.9. Surface morphology of the area with corrosion damage . Sample 47.